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Agricultural residues as precursors for activated carbon production—A review

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Abstract

A review of the production of activated carbons from agricultural residues is presented. The effects of various process parameters on the pyrolysis stage are reviewed. Influences of activating conditions, physical and chemical, on the active carbon properties are discussed. Under certain process conditions several active carbons with BET surface areas, ranging between 250 and 2410 m^2/g and pore volumes of 0.022 and 91.4 cm^3/g, have been produced. A comparison in characteristics and uses of activated carbons from agricultural residues with those issued from tires, and commercial carbons, have been made. A review is carried out of the reaction kinetic modelling, applied to pyrolysis of agricultural wastes and activation of their pyrolytic char.

Keywords: Activated carbons; Agricultural wastes; Pyrolysis; Activation; Modelling

Contents

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1. Introduction

Thermo-chemical processes such as pyrolysis or gasification have been widely applied to biomass, gain due to its energy content. Pyrolysis is one form of energy recovery process, which has the potential to generate char, oil and gas product [1]. Because of the thermal treatment, which removes the moisture and the volatile matter contents of the biomass, the remaining solid char shows different properties than the parent biomass materials. The remarkable differences are mainly in porosity, surface area, pore structures (micropores, mesopores and macropores) and physicochemical properties such as composition, elemental analysis and ash content [2]. These changes in the properties usually lead to high reactivity, and hence, an alternative usage of char as an adsorbent material becomes possible [1]. Thus, the char becomes an attractive by-product, with applications including production of activated carbons (ACs), which is useful as a sorbent for air pollution control as well as for wastewater treatment [3]. ACs are carbons of highly microporous form with both high internal surface area and porosity, and commercially the most common adsorbents used for the removal of organic compounds from air and water streams. They also often serve as catalysts and catalyst supports. The market is indeed vast.

The process parameters, which have the largest influence on the products of pyrolysis, are the particle size, temperature and heating rate. The process conditions can be optimized to maximize the production of the pyrolytic char, oil or gas, all of which have potential uses as fuels. Any cheap material, with a high carbon content and low inorganics,

Nomenclature

w	mass fraction of the solid present at any time/mass of actual sample at time t
t	time, s
k_0	pre-exponential factor, s^{-1}
E or $E\alpha$	activation energy, $kJ\,mol^{-1}$
$E_{\alpha 0}$	initial activation energy for $z = 0$, $kJ\,mol^{-2}$
R	universal gas constant, $kJ\,mol^{-1}K^{-1}$/reactivity, s^{-1}
T	instantaneous temperature/absolute temp, K
w_0	initial mass fraction/ mass of initial sample
w_{∞}	mass fraction at time infinity/mass of residue at the end/ residual mass fraction
r	rate of generation
m	loss of residue mass
m	total gas moles
A	pre-exponential factor or frequency factor, min^{-1}
C	concentration of the gas at the reactor outlet
F	total gas flow rate/ weight fraction of the less reactive phase
K_i	frequency factor/ the Arrhenius kinetic constant
k_{app}	reaction rate constant
V^{∞}	the ultimate attainable yield
V	volume of the system/initial bed volume
V_i	the percentage of volatiles in time t
p_{CO_2}	partial pressure of CO_2
w_{α}	the ash mass from the analysis of the initial sample
q	Constant heating rate
C_{co}	initial carbon molar bulk density of the sample
M_{0i}	initial mass of the sample i
m_{fi}	final mass of the sample in the reaction time j
m_{ij}	sample mass for the reaction i at time
W_0	weight of char
n	order of reaction
X	weight of sample undergoing reaction, kg/ratio of instantaneous weight of the char sample to the initial weight of the sample
k	rate constant of gas formation /specific rate constant
M	mass of residue
M_0	initial mass of residue to be pyrolyzed
T_{amb}	ambient temperature
z	normalized fractional conversion

Greek symbols

α	converted rate of the reaction
β	heating rate, designed by experiments/deactivation rate
γ	the order with respect to z

Subscripts

0	initial
∞	infinity
m	number of moles generated
i	component number
f	final

can be used as a raw material for the production of AC [4]; agricultural by-products have proved to be promising raw materials for the production of ACs because of their availability at a low price. They can be used for the production of AC with a high adsorption capacity, considerable mechanical strength, and low ash content [5]. Literature survey indicates that there have been many attempts to obtain low-cost AC or adsorbent from agricultural wastes such as *wheat* [6], *corn straw* [6], *olive stones* [7,8], *bagasse* [7,8], *birch wood* [7,8], *miscanthus* [7,8], *sunflower shell* [2], *pinecone* [2], *rapeseed* [2,9], *cotton residues* [2], *olive residues* [2], *pine rayed* [10], *eucalyptus maculata* [10], *sugar cane bagasse* [10,11], *almond shells* [5,12,13], *peach stones* [4], *grape seeds* [5], straw [7,8,14], *oat hulls* [3,15], *corn stover* [3,15], *apricot stones* [5,12], *cotton stalk* [1], *cherry stones* [5], *peanut hull* [16], *nut shells* [5,17–20], *rice hulls* [11], *corn cob* [4,21–23], *corn hulls* [15], *hazelnut shells* [12], *pecan shells* [11], *rice husks* [24,25] and *rice straw* [11,26].

The purpose of the present paper is the evaluation of the experimental data that were determined for various types of residues, reported in the literature. Moreover, understanding pyrolysis kinetics is important for the effective design and operation of the thermochemical conversion units. Given that solid devolatilization is always a fundamental step, Thermogravimetric analysis (TGA) technique has been applied in several cases. The present paper reviews also the models used to describe the process of AC production from agricultural wastes.

2. Experimental conditions for carbon production from agricultural wastes

2.1. Pyrolysis

Agricultural residues are produced in huge amounts worldwide, their proximate and ultimate analysis are presented in Table 1, while Table 2 presents some carbonization and activation conditions for the production of the ACs from agricultural residues.

Corn stover with oat hulls for activated carbon production by TGA was studied by Fan et al. [3]. There was no pre-treatment prior to fast pyrolysis that was held in a nitrogen fluidized bed reactor at a typical biomass feed of 7 kg/h. Zhang et al. [15], studied oak wood wastes, corn hulls and corn stover carbonization in a fluidized bed reactor at 500 °C. In the study of Haykiri-Acma et al. [2], TGA was used to pyrolyse and then gasifies chars obtained from sunflower shell, pinecone, rapeseed, cotton and olive residues pyrolysis. Obtained chars were heated in order to gasify under steam and nitrogen atmosphere and in equal volumetric ratio. For pinus radiate, eycalyptus maculate and sugar cane bagasse, atmospheric reactivity measurements were performed under isothermal conditions, using a thermogravimetric analyser [10]. The heat up was carried out at a nominal heating rate of 40 °C min^{-1}. Sugarcane bagasse, rice hulls, rice straw, and pecan shells were also

Table 1
Agricultural residues availability, proximate and ultimate analysis [91]

Agricultural wastes	Moisture %ww	Ash %ww	Volatiles %ww	C %ww	H %ww	O %ww	N %ww	S %ww	HHV kcal/kg
Olive tree prunings	7.1	4.75	n.a	49.9	6	43.4	0.7		4500
Cotton stalks	6	13.3	n.a	41.23	5.03	34	2.63	0	3772
Durum wheat straw	40	n.a	n.a	n.a	n.a	n.a	n.a	n.a	4278
Corn stalks	0	6.4	n.a	45.53	6.15	41.11	0.78	0.13	4253
Soft wheat straw	15	13.7	69.8	n.a	n.a	n.a	n.a	n.a	4278
Vineyward prunings	40	3.8	n.a	47.6	5.6	41.1	1.8	0.08	4011
Corn cobs	7.1	5.34	n.a	46.3	5.6	42.19	0.57	0	4300
Sugar beet leaves	75	4.8	n.a	44.5	5.9	42.8	1.84	0.13	4230
Barley straw	15	4.9	n.a	46.8	5.53	41.9	0.41	0.06	4489
Rice straw	25	13.4	69.3	41.8	4.63	36.6	0.7	0.08	2900
Peach tree prunings	40	1	79.1	53	5.9	39.1	0.32	0.05	4500
Almond tree prunings	40	n.a	n.a	n.a	n.a	n.a	n.a	n.a	4398
Oats straw	15	4.9	n.a	46	5.91	43.5	1.13	0.015	4321
Sunflower straw	40	3	n.a	52.9	6.58	35.9	1.38	0.15	4971
Cherry tree prunings	40	1	84.2	n.a	n.a	n.a	n.a	n.a	5198
Apricot tree prunings	40	0.2	80.4	51.4	6.29	41.2	0.8	0.1	4971

studied, [11], in an atmosphere of nitrogen gas at 750 °C using an inert atmosphere furnace with retort. Chars were activated until approximately 30% burn-off was achieved.

Pyrolysis temperature has the most significant effect-followed by pyrolysis heating rate, the nitrogen flow rate and then finally the pyrolysis residence time. Generally, increasing pyrolysis temperature reduces yields of both chars and ACs. According to f Putun et al. [1], increased temperature leads to a decreased yield of solid and an increased yield of liquid and gases. As the temperature is raised, there is a rise in ash and fixed carbon percentage and there is a decrease in volatile matter. Consequently, higher temperature yields charcoals of greater quality. The decrease in the char yield with increasing temperature could either be due to greater primary decomposition of biomass at higher temperatures or through secondary decomposition of char residue. The secondary decomposition of the char at higher temperatures may also give some non-condensable gaseous products, which also contributes to the increase in gas yield. Indeed, as the temperatures of primary degradation are increased or the residence times of primary vapours inside the cracked particle has to stay shorter, the char yields decrease [1]. Temperature also studied of Tsai et al. [4,21] for preparation of ACs with chemical activation ($ZnCl_2$), where it was noticed that char yield decreases with temperature, while soaking time has no effect on the char yield.

2.2. Activation

Basically, there are two main steps for the preparation and manufacture of AC: (1) the carbonization of the carbonaceous raw material below 800 °C, in the absence of oxygen, and (2) the activation of the carbonized product (char), which is either physical or chemical. The types of activation are represented in Table 3.

Table 2
Carbonization and activation conditions of agricultural residues

Reference	Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical treatment	Additional information
[6]	Wheat	100 µm	127–375 °C			
[6]	Corn straw	100 µm	127–375 °C			
[7,8]	Olive (steam)/(N_2)			750/2 (10 °C)	Steam/CO_2	One-step pyrolysis/activation
[7,8]	Straw (steam)/(N_2)			750/2 (10 °C)	Steam/CO_2	One-step pyrolysis/activation
[7,8]	Birch (steam)/(N_2)			750/2 (10 °C)	Steam/CO_2	One-step pyrolysis/activation
[7,8]	Bagasse (steam)/(N_2)			750/2 (10 °C)	Steam/CO_2	One-step pyrolysis/activation
[7,8]	Miscanthus (steam)/(N_2)			750/2 (10 °C)	Steam/CO_2	One-step pyrolysis/activation
[2]	Sunflower shell	<0.250 mm	1000 °C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing
[2]	Pinecone	<0.250 mm	1000 °C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing
[2]	Rapeseed	<0.250 mm	1000 °C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing
[2]	Cotton refuse	<0.250 mm	1000 °C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing
[2]	Olive refuse	<0.250 mm	1000 °C	1000 °C	Steam	Gasification up to 1000 °C after pyrolysing
[10]	Radiata pine	1–2 mm	950 °C (20 °C/s)			Suite of rectors (a wire mesh reactor, a tubular reactor and a drop tube furnace)
[10]	Eycalyptus	1–2 mm	950 °C (20 °C/s)			Suite of rectors (a wire mesh reactor, a tubular reactor and a drop tube furnace)
[10]	Sugarcane bagasse	1–2 mm	950 °C (20 °C/s)			Suite of rectors (a wire mesh reactor, a tubular reactor and a drop tube furnace)
[11]	Sugarcane bagasse	10–20 mesh and 12–40 mesh	750 °C/1	900/4 and 20	CO_2/N_2	
[5]	Apricot stones/product	0.2–1 mm	800/1 h (15 °C/min)	800/1 h	Steam	One-step pyrolysis/activation
[12]	Apricot stones	1–1.25 mm		800/18	Chemical ($ZnCl_2$)	
[5]	Cherry stones/product	0.2–1 mm	800/1 h (15 °C/min)	800/1 h	Steam	One-step pyrolysis/activation

Table 2 (*continued*)

Reference	Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical treatment	Additional information
[5]	Grape seeds/product	0.2–1 mm	800/1 h (15 °C/min)	800/1 h	Steam	One-step pyrolysis/activation
[5]	Nut Shells/product	0.2–1 mm	800/1 h (15 °C/min)	800/1 h	Steam	One-step pyrolysis/activation
[17]	Pistachio-nut shells	2.0–2.8 mm	500/2 (10 °C/min)	900/30 min (10 °C/min)	Physical CO_2	
[19]	Pistachio-nut shells	1–2 mm	500/2	800/2.5 (10 °C/min)	Physical CO_2	Two-step physical method
[18]	Macadamia nutshell	212–300 μm	1 h	500	Chemical ($ZnCl_2$)	Chemical activation with both $ZnCl_2$ and KOH
		212–300 μm	1 h	800	Chemical (KOH)	
[12]	Hazelnut shell	1–1.25 mm		750/10	Chemical ($ZnCl_2$)	
[16]	Peanut hulls	n.a.	500/2	700–900 °C	Physical	Two-step process
		n.a.	—	600/2	Pure steam	One-step process
		n.a.	—	300–750/6	Chemical ($ZnCl_2$)	
		n.a.	—	500–700/3	Chemical (KOH)	
		n.a.	—	500/3–6	Chemical (H_3PO_4)	
[12]	Almond shells	1–1.25 mm		750/10	Chemical ($ZnCl_2$)	
[20]	Almond shells	n.a.			Chemical (H_3PO_4)	
[5]	Almond shells/product	0.2–1 mm	800/1 h (15 °C/min)	800/1 h	Steam	One-step pyrolysis/activation
[13]	Almond shells	1.5–2 mm	400/1	850/1	Physical	Different samples (either with CO_2 or N_2)
[3]	Oat hulls	<1 mm	500 °C/(1.5 s residence)	800/30 min	Steam	
				800/60 min	Steam	
				800/90 min	Steam	
				800/120 min	Steam	
[4]	Corn cob	1.435 mm	400–800	—	Chemical ($ZnCl_2$)	The impregnation ratio yluctuates 20–175%wt
[21]	Corn cob	1.44 mm	500/0.5 h soak. time	—	Chemical ($ZnCl_2$)	Carbonization and activation are carried out simultaneously, optimal soaking time and temperature, impregnation ratio 175wt%
		1.44 mm	500/2 h soak. time	—	Chemical ($ZnCl_2$)	Carbonization and activation are carried out simultaneously

		1.44 mm	700/0.5 h soak. time	—	Chemical ($ZnCl_2$)	Carbonization and activation are carried out simultaneously
		1.44 mm	700/2 h soak. time	—	Chemical ($ZnCl_2$)	Carbonization and activation are carried out simultaneously
		1.44 mm	800/0.5 h soak. time	—	Chemical ($ZnCl_2$)	Carbonization and activation are carried out simultaneously
		1.44 mm	800/2 h soak. time	—	Chemical ($ZnCl_2$)	Carbonization and activation are carried out simultaneously
[22]	Corn cob	1.19–1.68 mm	500–800/1 h soak. time	—	Chemical (KOH)	Chemical and physical activation
		1.19–1.68 mm	500–800/1 h soak. time	—	Chemical (K_2CO_3)	Chemical and physical activation
[23]	Corn cob	0.5–2 mm	500/2	850/1	Steam	Physical activation/two-steps
		0.5–2 mm		500/2	Chemical (H_3PO_4)	Chemical activation
		0.5–2 mm		600–700/2	Pure steam	Steam-pyrolyzed/one-step scheme
[14]	Straw/Char	5.97 mm	550 (fluidized bed)			20t/h raw material
[1]	Cotton stalk	0.25–1.8 mm(1.2)	400 °C			Increase of residence time result in formation of activated carbon
			500 °C			400–700 with 7 °C/min
			550 °C			400–00 with 7 °C/min
			700 °C			400–00 with 7 °C/min
[15]	Oak/oak char			700/1		
				700/2		
				800/1		
				800/2		
[15]	Corn hulls/corn hulls char			700/1		
				700/2		
				800/1		
				800/2		
[15]	Corn stover/char			700/1		
				700/2		
				800/1		
				800/2		
[3]	Corn stover	<1 mm	500 °C/(1.5 s residence)	800/30 min	Steam	
				800/60 min	Steam	
				800/90 min	Steam	
				800/120 min	Steam	

Table 2 (*continued*)

Reference	Raw material	Particle size	Carbonization conditions (°C/h)	Activation conditions (°C/h)	Chemical treatment	Additional information
[27]	Olive-seed/char	125–160 μm	800/1	800/1 800/2 900/1 900/2	Chemical (KOH)	
[109]	Olive-waste cakes	0.1–10 mm	400/1	750–850/30–70 min	Steam	Optimal conditions: 68 min and 822°C. Great adsorption capacity and high surface area
[26]	Rice-straw	ca.3 cm	700–1000/1 (10 °C/min)	900	KOH	Two-stage method
		ca.3 cm		500–900/1(10 °C/min)	Chemical (KOH)	One-stage method
[11]	Rice-straw	10–20 mesh and 12–40 mesh	750/1	900/4 and 20	CO_2/N_2	
[24]	Rice-husk	200–16 mesh	400/1	600/1	Steam activation	
[25]	Rice-husk	n.a.		600/3	$ZnCl_2/CO_2$	Different salt solutions/CO_2 partcipated to the activation method
[11]	Rice-hulls	10–20 mesh and 12–40 mesh	750/1	900/4 and 20	CO_2/N_2	
[11]	Pecan shells	10–20 mesh and 12–40 mesh	700–800/1	800/2–8	Physical	
		10–20 mesh and 12–40 mesh		450/1	Chemical	
[20]	Pecan shells	n.a.			Chemical (H_3PO_4)	
		n.a.			Steam	
[28]	Cassava peel	n.a.		750	Chemical (KOH)	For 3 h and 650 °C $S_{BET} = 1183\ m^2/g$, impregnation ratio 1:1

Table 3
Types of activation

Activation	Steps of process	Reference	Material
Physical	Two-steps	[2,11,13,15–17,19,23,24,26,109]	Pistachio-nutshells, sunflower shells, pinecone, rapeseed, cotton residues, olive residues, peanut hulls, almond shells, oak, corn hulls, corn stover, rice straw, rice husk, rice hulls, pecan shells, sugarcane bagasse, olive-waste cakes
Chemical	One-step	[4,12,16,18,20–23,25–28]	Corn cob, olive seeds, rice husks, rice straw, cassava peel, pecan shells, Macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells
Steam-Pyrolysis	One-step	[3,5,7,8,16,23]	Olive, straw, birch, bagasse, miscanthus, peanut hulls, corn stover, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls

Table 4
Physical activation of agricultural residues, reported in the literature

Activating agent	Reference	Material
Steam	[2,23,24,109]	Rice husk, corn cob, olive residues, sunflower shells, pinecone, rapeseed, cotton residues, olive-waste cakes
CO_2	[11,15,17,19]	Oak, corn hulls, corn stover, rice straw, rice hulls, pecan shells, Pistachio nutshells, sugarcane bagasse
	[13,16]	Peanut hulls, almond shells

2.2.1. *Physical activation*

Physical activation is a two-step process. It involves carbonization of a carbonaceous material followed by the activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air or their mixtures, as it can be seen in Table 4. The activation gas is usually CO_2, since it is clean, easy to handle and it facilitates control of the activation process due to the slow reaction rate at temperatures around 800 °C [15]. Rice husk, corn cob, oak, corn hulls, corn stover, rice straw, rice hulls, pecan shells, peanut hulls and almond shells [2,11,13,15,16,17,19, 23,24,25,26], were the raw materials studied by this method. Carbonization temperature range between 400 and 850 °C, and sometimes reaches 1000 °C, and activation temperature range between 600 and 900 °C.

The activated carbons produced by physical activation did not have satisfactory characteristics in order to be used as adsorbents or as filters.

Physical activation of oak, corn hulls and corn stover chars [15], was performed at temperatures of 700 and 800 °C and durations of 1 and 2 h. For oak, the longer the

activation duration, the greater the adsorption capacity of the resultant ACs, and vice-versa for the corn hulls and corn stover. Apparently, the activation durations of 1 and 2 h did not appreciably affect the properties of ACs from oak at 700 °C. In contrast, the surface areas, total pore volume, and pore volume of AC obtained upon 1 h of activation were much less than those upon 2 h of activation at 800 °C. Obviously, the pore structure of carbons from oak altered substantially for different durations of activation at 800 °C. The surface areas and pore volumes of ACs from chars generated from corn hulls as well as from corn stover were appreciably greater after 1 h of activation than after 2 h of activation. This was in sharp contrast to the results from the activation of char from oak. Plausibly, in activating the chars from both corn hulls and corn stover, the rate of pore structure formation exceeded that of the destruction due to the pore enlargement and collapse at the earlier stage and vice versa at the later stage. A more thorough research for corn cobs was made by Abdel-Nasser et al. [23]. The char was carbonized at 500 °C, then soaked for 2 h, and steam-activated at 850 °C in a flow of steam/N_2, for 1 h.

2.2.2. Chemical activation

In the *chemical* activation process the two steps are carried out simultaneously, with the precursor being mixed with chemical activating agents, as dehydrating agents and oxidants. Chemical activation offers several advantages since it is carried out in a single step, combining carbonization and activation, performed at lower temperatures and therefore resulting in the development of a better porous structure, although the environmental concerns of using chemical agents for activation could be developed. Besides, part of the added chemicals (such as zinc salts and phosphoric acid), can be easily recovered [4,15,21]. However, a two-step process (an admixed method of physical and chemical processes) can be applied [26], Table 5.

Chemical activation was used in most of the studies for corn cob, olive seeds, rice husks, rice straw, cassava peel, pecan shells, Macadamia nutshells, hazelnut shells, peanut hulls, apricot stones, almond shells [4,12,16,18,20,21,22,23,25–28]. The most common chemical agents are $ZnCl_2$, KOH, H_3PO_4 and less K_2CO_3. As it can be seen almond shells, hazelnut shells and apricot stones [12], were activated with a solution of $ZnCl_2$ (30 wt%) at 750–800–850 °C, respectively, for 2 h. Zinc chloride was also used in the study of Tsai et al. [4,21], for the activation of carbons from corn cob in the range of 400–800 °C, for 0.5–4.0 h of soaking time, and as well in the study of Badie et al. [16], where a 50% solution was mixed with sample of peanut hulls at 300–750 °C for 6 h. Additionally, $ZnCl_2$ was used as an activating agent for Macadamia nutshells [18], and rice husks [25], at 500 °C for 1 h, and

Table 5
Chemical activation of agricultural residues

Activating agent	Reference	Material
$ZnCl_2$	[4,12,16,18,21,25]	Corn cob, Macadamia nutshells, peanut hulls, almond shells, hazelnut shells, apricot stones, rice husks
KOH	[16,18,22,26–28]	Corn cob, Macadamia nutshells, peanut hulls, olive seed, rice straw, Cassava peel
H_3PO_4	[16,20,23]	peanut hulls, almond shells, pecan shells, corn cob
K_2CO_3	[22]	Corn cob

at 600 °C for 3 h in combination with CO_2, respectively, and gave the best characteristics of the activated carbons than with any other agent (chemical or physical).

Carbons from Macadamia nutshells [18], and peanut hulls [16], were activated with KOH at 800 °C for 1 h and 500–700 °C for 3 h, respectively. *ACs that were produced, did not have good quality as the ones produced with $ZnCl_2$.* Corn cob char [22], that was activated with KOH at 500–800 °C for 1 h, did not generally give AC with such good S_{BET}. Activation of olive seed carbons [27], took place at 800–900 °C for 1–2 h and gave ACs with high surface area and char yield. For rice straw char [26], activation proceeded firstly in one-stage at 500–900 °C for 1 h and secondly in two-stages, at 700–1000 °C for 1 h (carbonization conditions) and then at 900 °C for the activation. Cassava peel char [28], activated at 650 and 750 °C, the higher S_{BET} appeared in the second case.

From the results, it became very obvious that the two-stage process was much more effective, as it gave ACs with higher porosity. In fact, this method (two-step chemical activation process), gave the higher surface area from all the studies being mentioned in the present review.

Activation with H_3PO_4 was used for carbons from peanut hulls [16], corn cob [23], almond shells and pecan shells [20]. The activating conditions for peanut hull chars were 500 °C for 3 h, while for corn cob chars 500 °C for 2 h. Corn cob gave better characteristics of the ACs in the respective research than peanut hull. Almond shell chars activated with H_3PO_4 gave carbons with a little lower surface area than those mixed with $ZnCl_2$.

Carbons from corn cob [22], were activated with K_2CO_3 at 500–800 °C for 1 h, where the ACs produced, comparatively with the results with KOH, had a lower surface area and gave the maximum char yield.

2.2.3. Steam pyrolysis/activation

There is also an additional one-step treatment route, denoted as *steam-pyrolysis* (see Table 6) as reported [3,5,7,8,16,23], where the raw agricultural residue is either heated at moderate temperatures (500–700 °C) under a flow of pure steam, or heated at 700–800 °C under a flow of just steam. The residues studied with this method were olive, straw, birch, bagasse, miscanthus, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls, corn stover, and peanut hulls. The samples in the study of Minkova et al. [7], were heated with a heating rate of 10 °C/min to a final temperature of 700 °C, 750 °C or 800 °C and kept 1 or 2 h at this temperature in the flow of steam, while the final carbonization temperature in the study of Savova et al. [5] was 800 °C for 1 h.

For the preparation and characterization of AC derived from oat hulls or corn stover [3], char was heated at 800 °C for 30, 60, 90 and 120 min. The ACs, which had a high pore volume, were weighed to determine activation burn-off or mass loss due to activation.

Table 6
Steam-pyrolysis activation in one-step process of agricultural residues

	Reference	Material
Steam	[3,5,7,8]	Olive, straw, birch, bagasse, miscanthus, apricot stones, cherry stones, grape seeds, nutshells, almond shells, oat hulls, corn stover
Pure steam	[6,23]	Peanut hulls, corn cob

The burn-off refers to the weight difference between the original char and the AC divided by the weight of original char with both weights on a dry basis. The following relationship is used for calculating the activation burn-off of biomass-derived chars:

Activation burn-off % = 100−{[mass after activation (g)/original mass (g)] × 100}

$$\Rightarrow \text{burn-off} = \frac{W_0 - W_1}{W_0} \times 100\%,$$

where W_0 is the weight of char and W_1 the mass of the carbon after activation.

The activated carbons, produced *by steam* gasification, were generally proved to be weakly affective, except the ones from almond shell, apricot and cherry stones [5].

3. Properties and characteristics of agricultural residues issued active carbons

3.1. Surface area

The BET surface area of char is important because, like other physico-chemical characteristics, it may strongly affect the reactivity and combustion behaviour of the char. The chars from pyrolysis above 400 °C had a surface area and a high surface area formed [1]. In the study of Tsai et al. [4,21] surface areas were observed to decrease at higher pyrolysis temperature and soaking time. The higher surface areas are probably due to the opening of the restricted pores. The percentage of micropore followed the increase of pyrolysis temperature, but this rate of increase was not as fast as the rate of declination in surface areas. The BET surface areas which calculated in the research of Tsai et al. [4,21] were observed to increase at higher activation temperature, for both KOH and K_2CO_3 series, and the maximum rate of increase in BET surface area occurred between 650 and 700 °C.

3.2. Pore size and volume

Both the size and distribution of micropores, mesopores and macropores determine the adsorptive properties of ACs. For instance, small pore size will not trap large adsorbate molecules and large pores may not be able to retain small adsorbates, whether they are charged, polar molecules or uncharged, non-polar compounds [20].

Materials with a greater content of lignin (grape seeds, cherry stones) develop ACs with macroporous structure, while raw materials with a higher content of cellulose (apricot stones, almond shells) yield AC with a predominantly microporous structure [5].

The pore size, in the study of Tsai et al. [4,21] which was with chemical activation with $ZnCl_2$, was calculated on the basis of desorption data by employing the Barrett–Joyner–Halenda (BJH) method. As it can be observed in Tables 7 and 8, the total pore volume is decreasing not only with the increase of the temperature, but also with the increase of the soaking time when the temperature is constant. On the contrary, in the research of Tsai et al. [4,21] the values of total pore volume increase rapidly with increase in the activation temperature. It is noted that the maximum values (i.e. 0.87 and 0.74 cm^3/g for 15 wt% KOH and 37.5 wt% K_2CO_3 ACs, respectively) of total pore volume at 800 °C, are larger than those of commercial ACs, i.e. 0.60 and 0.52 cm^3/g for BPL and PCB, respectively, (Calgon Carbon Co., Pittsburgh, USA).

Table 7
Characteristics of activated carbons from agricultural residues

Reference	Raw material	S_{BET} (m^2/g)	V_o (cm^3/g)	Yield (%)
[5]	Apricot stones	1190	0.50	18.2
[5]	Cherry stones	875	0.28	11.2
[5]	Grape seeds	497	0.12	26.2
[5]	Nut Shells	743	0.21	17.9
[17]	Pistachio-nut shells	778	0.466	
[18]	Macadamia nutshell	1718	0.723	
		1169	0.529	
[16]	Peanut hulls	80.8–97.1	0.022–0.043	30
		253	0.079	29
		420	0.173	30
		228–268	0.033–0.076	27–32
		240–1177	0.036–0.57	22–36
[5]	Almond shells	998	0.40	17.8
[13]	Almond shells	1005.7–1217.7, 1157.4–1315.4		15.84–6.34
[3]	Oat hulls	349	91.4	
		431	88.4	
		522	86.8	
		625	84.2	
[4]	Corn cob	400–1410	0.19–0.70	
[21]	Corn cob	960	0.486	28.8
		774	0.349	30.4
		747	0.368	27.8
		682	0.335	29.2
		706	0.345	27.8
		721	0.342	28.2
[22]	Corn cob	0.1–1.806		12.8–31.3
		0.2–1.541		17.4–33.5
[23]	Corn cob	607	0.296	8.7
		960	0.629	18.3
		618–786	0.321–0.430	20.1–20.8
[14]	Straw			
[1]	Cotton stalk	37.28		30.30
		3.33		29.17
		3.32		27.93
		3.14		25.56
[15]	Oak	642	0.2704	
		644	0.2450	
		845	0.3212	
		985	0.3792	
[15]	Corn hulls	977	0.3352	
		902	0.3284	
		1010	0.4348	
		975	0.3792	
[15]	Corn stover	660	0.2817	
		432	0.1818	
		712	0.2849	
		616	0.2343	
[3]	Corn stover	424	88.7	
		442	86.2	
		374	85.0	
		311	84.2	

Table 7 (*continued*)

Reference	Raw material	S_{BET} (m^2/g)	V_o (cm^3/g)	Yield (%)
[27]	Olive-seed	1339		76
		1334		72
		1550		65
		1462		59
[109]	Olive-waste cakes	514–1271	0.217–0.557	
[26]	Rice-straw	2410	1.4	
[25]	Rice-husk	480	13.652	
[20]	Pecan shells	682		32
		724		18
[28]	Cassava peel	1378	0.583	

Table 8
Characteristics of activated carbons from tires [92]

Reference	Raw material	S_{BET} (m^2/g)	V_o (cm^3/g)	Yield (%)
[93]	Tire	431		33
[56]	Used automotive tires	1260		9
		600		22
[94]	Scrap tires	607	0.01	12.3
		553	0.07	16.6
[95]	Used tires	813		17
		793		16.5
[96]	Waste tire rubber	1000	0.44	4
		978	0.48	4.6
[97]	Used tires	640		13.6
[98]	Waste tires	474	0.23	16
		411	0.19	12
[100]	Used tires	528		19.5
		478		17.2
[102]	Waste tires	1031	0.28	10
[102]	Scrap tires	164	0.04	29.5
[104]	Scrap tires	820	0.27	
		1031	0.28	
		888	0.25	
[54]	Waste tires	1119	0.57	7.9
		1177	0.54	11.2
[55]	Waste tire rubber	1070	0.55	15.1
		1022	0.54	17.9

All the characteristics from the ACs produced are summed up in Table 7. As it can be seen carbons from corn stover and oat hulls [3], give the bigger pore volume, whereas olive seed carbons [27], when being activated have high percentage of char yield (76%). The higher S_{BET} (2410 m^2/g) can be taken by pyrolyzing rice straw [26], and activate the carbons with KOH, but remarkable surface areas can also be taken from corn cob [22], olive seed [27], and Cassava peel [28].

4. Applications and uses of agricultural based active carbons

ACs concern many industries as diverse as food processing, pharmaceuticals, chemical, petroleum, mining, nuclear, automobile and vacuum manufacturing, because of their adsorptive properties they have due to a high available area which is presented in their extensive internal pore structure. Such high porosity is a function of both the precursor as well as the scheme of activation [23].

The chemical nature of ACs significantly influences its adsorptive, electrochemical, catalytic, and other properties. Generally speaking, ACs with *acidic* surface chemical properties are favourable for basic gas adsorption such as ammonia while ACs with *basic* surface chemical properties are suitable for acidic gas adsorption such as sulphur dioxide [19]. The uses of the AC produced by agricultural residues are summarized in Table 9.

4.1. In gas phase adsorption

The resulting ACs may be used as adsorbent for air pollution control, as it can effectively treat industrial gas, and indoor air environments [21]. Due to their large number of micropores and the high surface area (high adsorption capacities) they can be used as catalysts for gas purification, separation and deodorization.

Adsorption by commercial ACs offers an efficient technology for removing volatile organic compounds (VOCs) from air pollution sources, owing to their large specific surface areas, high micropore volumes and rapid adsorption capabilities [29]. Furthermore, several microporous ACs from various manufacturers were selected to study the viability of using

Table 9
Uses of activated carbons produced by agricultural residues

Reference	Uses	Raw material
[13]	Treat industrial gas, indoor air (air pollution control)	
[18,25]	Adsorption of mathylene blue (liquid purification)	Peanut hulls, rice straw
[20]	Trace metals	
[24,46,39,40]	adsorption of acid dyes	Rice husk, orange peel
[41,42]	Removal of ions	Palm kernel fibre
[44]	Removal of Arsenic	
[51,52]	Adsorption of atrazine	Pitch-based carbons
[53]	Clean-up of fruits and vegetables	Activated carbons membranes
[47,48,49,50]	Removal of nitrate and pesticides	Wheat straw
[45]	Be as support for noble metals/catalysts per se	
[33]	Wastewater treatment	Rice husks
[36]	Groundwater treatment	Jordanian olive stones
[34,35]	Purification of drinking water	
[39,40]	Removal of heavy metals	
[30]	Purification of effluent gas streams	
[32]	Removal of mercury vapours	
[29]	Removal of volatile organic compounds	
[31]	Removal of NO_x and SO_x	
[37,38]	Removal of phenols and phenolic compounds	

monolithic adsorption units, capable of regeneration for the purification of effluent gas streams [30].

The removal processes for SO_x and NO_x can be designed using activated carbon fiber (ACF) for the environment of busy traffic crossings, parking spaces, and large halls as well as for exhaust gases such as the flue gas from a power plant, catalyst regeneration for fluidized catalytic cracking (FCC) process, and ventilated gas from motorway tunnels [31]. Activated carbon are also used for removing mercury vapours from a gas mixture containing H_2S, O_2 and moisture that is representative of the exhaust gas emissions of the geothermal power plants [32].

4.2. In liquid phase adsorption

Liquid phase adsorption applies to many purification processes, one of the most relevant been the wastewater treatment (e.g. by rice husk carbons [33]), the drinking water [34], and the industrial effluents purification [35], and ground water treatment (Jordanian olive stones [36]).

Adsorption of methylene blue has been one of the most important means of assessing removal capacity from the aqueous phase. Phosphoric acid-ACs are the best in the uptake of methylene blue from aqueous solution (200–400 mg/g) [16]. Porous carbons with high surface area and adsorption capacities for methylene blue and iodine could be obtained from a rice straw precursor [26], particularly by the two-stage method, in which the raw rice straw is carbonized at the first stage and activated with KOH at the subsequent stage. From the one-stage method the porous of only moderate performance could be obtained, because the ash-formation makes it difficult to increase the optimum temperature at which micropores can be created.

ACs are used for the removal of phenols, phenolic compounds [37,38], heavy metals and dyes [39,40], met al ions [41,42] and mercury (II) [43] from aqueous solutions. Phenolic derivatives belong to a group of common environmental contaminants. The presence of their even low concentrations can be an obstacle to the use (and/or) reuse of water. Phenols cause unpleasant taste and odour of drinking water and can exert negative effects on different biological processes. Phenolic derivatives are widely used as intermediates in the synthesis of plastics, colours, pesticides, insecticides, etc. Degradation of these substances means the appearance of phenol and its derivatives in the environment [37]. They can also adsorb arsenic (As) [44] and trace metals [20] from drinking water, or be used as support for noble metals or as catalysts per se in liquid phase reactions [45].

Adsorption of acid dyes from aqueous solution, like acid violet 17 from waste waters, by orange peel carbons [46], or acid yellow 36 by rice husk carbons [24], is one of the most efficient methods. Carbons with low dye uptake (30–100 mg/g) are those chemically activated with $ZnCl_2$, KOH, steam pyrolyzed or chars [16].

4.3. Active carbon for organics-pesticides

ACs are very efficient in the adsorption of nitrate and pesticides from surface waters [47–50]. Pitch-based AC fibres are more effective in the atrazine removal dynamic tests than granular activated carbon if they are highly activated. The rapid adsorption kinetics of the atrazine with the highly activated ACF seems to be the main reason for its having a better performance than granular AC (GAC). This means that a fiber-type structure with

micropores directly accessible from the surface is not enough reason to justify the good efficiency of ACF [51]. Another carbon based material, Nyex 100 [52], was also used for the removal of atrazine to low levels, below 1 μg^{-1}.

The feasibility of using AC membranes as the solid phase for an on-line single step extraction-cleanup of fruits and vegetables for multi residue screening was studied in [53]. The type of carbon present in these membranes (an acid-washed coconut charcoal) seems to be able to discriminate between compounds containing benzene rings with small substituents from those with bulky substituents. The origin of this selectivity may be due to the presence of active sites on the carbon surface. It is speculated that these sites are electron deficient sites, which could be deactivated by exposure to reducing agents, such as ascorbic acid. This is a property that could be exploited in the cleanup of samples for the isolation of compounds such as polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) from complex matrices such as soils and sediments.

4.4. Comparisons of active carbons

Making a comparison among various waste-issued ACs, those obtained from agricultural are much better than those produced by another abundant waste such as used tires. As it can be observed in Table 8, waste tires and wastes tires rubber [54,55], give also high pore volumes.

However, using tires as raw material to produce ACs, the higher surface area that can be taken is 1260 m^2/g [56], and somehow it is lower than that obtained from agricultural residues.

Uses of tire-based carbons are concentrated in Table 10. Generally, they can be used to adsorb phenols, p-chlorophenols, dyes, metals, lead, copper and chromium for the purification of drinking water and water treatment. They are suitable for the separation, storage and catalysis of gaseous species, and air pollution control (flue gas treatment). It was also found that steam-ACs have better adsorption capacity for dye (Black 5) and slightly lower phenol adsorption capacity in comparison with commercial carbons [54]. If the activation is made with CO_2 the capacity for phenol and methylene blue is almost the same to that of the commercial carbons [57].

Commercial carbons can be used satisfactory enough, as post treatment in order to adsorb colour, nitrate and dissolved organic carbon from drinking water, effluent water [47].

Table 10
Uses of activated carbons produced by tires

Reference	Uses
[96]	Adsorption of mercury (flue gas treatment), storage of natural gas and other flammable gases
[98]	Removal of halogenated hydrocarbons and pesticides (drinking water)
[57]	Adsorption of phenols, basic dyes and metals, water treatment (lead, copper)
[99]	Adsorption of phenols, *p*-chlorophenols, dyes (water treatment)
[100,101]	Storage of natural gas and other flammable gases, adsorption of SO_2 and butane
[103,54,105]	Adsorption of reactive dyes, phenols
[104,106]	Storage of natural gas and other flammable gases
[107]	Removal of chromium
[108]	Removal of organic and inorganic species (industrial effluents)

Table 11
Uses of commercial activated carbons

Reference	Active carbon	Uses
[48]	PAC/Chemviron	Dodine (surface waters)
[49]	ACF/Spectra corp	Atrazine (kinds of pesticides for water waste treatment)
[52]	Nyex 100	Atrazine (aqueous solutions)
[50]	ACF/KF-175, TOYOBO	Organic chlorine pesticides (water samples)

Organic pollutants, like different kind of pesticides, are also being removed by either powdered or granular or fiber ACs. Kouras et al. [48], showed that powdered active carbon produced by Chemviron was very effective in cleaning surface waters by the adsorption of dodine. The result was even better when using coagulants (polyelectrolyte, Al, Fe). The highest removal observed when mixing 50 mg/l PAC with ferric chloride (>98.2%). Ayranci et al. [49], supported that ACF, and especially pitch-based, was more effective in the removal of atrazine than granular AC. In their tests for waste-water purification it turned up that ACF (from Spectra corp.) had very high specific surface area, adsorption capacity and mechanical strength. A new collection method of organic chlorine pesticides in water samples (rainwater, river water, seawater) using an ACF filter (KF-175, TOYOBO) was proposed in the study of Murayama et al. [50], to be effective and economical compared to those by the conventional method. Finally, Brown et al. [52], used a novel carbon-based adsorbent material (Nyex 100) for the removal of atrazine to low levels, below $1\,\mu g l^{-1}$, from aqueous solutions, which regenerated electrochemically, and has the ability to reach three times greater adsorptive capacities than originally achieved. This material does not have internal surface and porous, and it has low cost. Table 11 summarizes the uses of commercial active carbons.

5. Review of the activated carbon formation from agricultural residues

The formation of AC from agro wastes consists of two steps: pyrolysis under nitrogen or other inert gases to break down the cross-linkage between carbon atoms, followed by activation in the presence of activating agents such as carbon dioxide or steam for further pore development (physical activation). The kinetic study of the process becomes a very important aspect towards the optimization of the process.

5.1. Kinetic models for pyrolysis

Biomass pyrolysis is generally a complex process that is why it is difficult to discover kinetic models that explain the mechanism of thermal decomposition. In many of kinetic formulations of *solid state reactions*, it has been assumed that the *isothermal homogeneous gas* or *liquid phase kinetic* equation can be applied. So, for a *single reaction at any time*, the kinetic equation to describe the thermal decomposition can be written as [58]:

$$\frac{dw}{dt} = k_0 \exp\left(-\frac{E}{RT}\right)f(w), \tag{1}$$

where w is the mass fraction of the solid and the function $f(w)$ *depends on the mechanism of the thermal decomposition.* Eq. (1) is usually expressed in terms of the parameter α defined as

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty}, \tag{2}$$

where w is the mass fraction present at any time, w_0 is the initial mass fraction and w_∞ is the mass fraction at time infinity. Thus the kinetic equation for *a single reaction* can be written as

$$-\frac{d_\alpha}{d_t} = k_0 \exp\left(-\frac{E}{RT}\right) f(\alpha). \tag{3}$$

A single reaction and first-order kinetics was also considered by Zabaniotou et al. [59]. Eq. (4) is the one that described their model:

$$\frac{\mathrm{d}V_i}{\mathrm{d}t} = K_i (V^\infty - V_i)^n, \tag{4}$$

$$K_i = k_{0i}\, \mathrm{e}^{E_i/RT},$$

where V_i is the percentage of volatiles in time t, V^∞ the ultimate attainable yield, K_i the Arrhenius kinetic constant, k_{0i} the pre-exponential factor, E_i activation energy.

However, in view of the fact that agricultural residues are mixtures which are mainly composed of cellulose, semicellulose and lignin, their decomposition *comprise a large number of reactions in parallel and in series.* Thus, the number of reactions that occur simultaneously in the most simple pyrolysis process is so great that it is practically impossible to develop a kinetic model that takes into account all these reactions. To overcome this difficulty, pyrolysis is usually studied in terms of *pseudo-mechanistic models* [58].

There are studies that assume a *first-order* reaction model *isothermal* or non-*isothermal* [58–63] and studies of *n-order* reactions [64,65], mostly non-isothermal. TGA or Deferential Thermogravimetric Analysis (DTG) method was used in different cases. A *deactivation model* (DM) [62,65], approximate integral method (AIM) [65] and *ASEM* (semi-empirical model) [66] were also studied. Tables 12 and 13 are summary of kinetic models on agricultural residues pyrolysis published in recent years. Table 14 summarizes kinetic parameters of various agro residues pyrolyis, published in recent years.

In this study, there has been an effort to classify various published models in three main categories:

(a) Models including only kinetic equations.
(b) Semi-empirical model.
(c) Models coupling kinetics and transport phenomena in a single biomass particle.

5.1.1. Models considering kinetic equations

The models of this category (published in the international literature) are divided into two main sub-categories, according to the heating conditions, as follows.

Table 12
Kinetic models for pyrolysis of agricultural residues

Reference		
Encinar et al. [60] First-order isothermal	$r=\frac{d_m}{d_t}$	(5)
	$m=\int_0^t CF d_t$	(6)
	$-\frac{d_M}{d_t}=kM$	(7)
	$m=\int_0^t CF\, d_t=\alpha(M_0-M)$	(8)
	$\frac{d_m}{d_t}=-\alpha\frac{d_M}{d_t}=\alpha kM=\alpha k\frac{m-\alpha M_0}{-\alpha}=k(m_0-m)$	(9)
	$\ln\frac{m_0}{m_0-m}=kt$	(10)
Cao et al. [61] First-order non-isothermal	$\frac{d_\alpha}{d_t}=k(1-\alpha)^n$	(17)
	$k=A\mathrm{e}^{-E/RT}$	(18)
	$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=-\frac{\mathrm{d}w}{\mathrm{d}T}=\frac{A}{\beta}\,\mathrm{e}^{-E/RT}\,(1-\alpha)^n$	(19)
	$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)=\ln\frac{A}{\beta}-\frac{E}{RT}+n\,\ln(1-\alpha)$	(20)
	$\Delta\,\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)=-\frac{E}{RT}\,\Delta\left(\frac{1}{T}\right)+n\Delta\ln(1-\alpha)$	(21)
	$\frac{[\Delta\ln(\mathrm{d}\alpha/\mathrm{d}T)]}{\Delta\ln(1-\alpha)}=\frac{[(-E/R)\,\Delta(1/T)]}{\Delta\ln(1-\alpha)}+n$	(22)
Bonelli et al. [62] First-order non-isothermal	$T=T_{\mathrm{amb}}+ut$	(25)
	$-\frac{\mathrm{d}w}{\mathrm{d}t}=k(w-w_\infty)$	(26)
	$k=k_0\,\exp\left(\frac{-E}{RT}\right)$	(27)
	$k_{\mathrm{app}}=k_0\,\exp\left\{\frac{-E_{\mathrm{a0}}(1+\beta Tz^\gamma)}{RT}\right\}$	(28)
	$z=1-\frac{w}{1-w_\infty}$	(29)

Table 12 (*continued*)

Reference		
Green and Feng [66] ASEM & traditional	$Y(T) = W[L(T)]^p[F(T)]^q$	(37)
Mansaray and Ghaly [64]	$\frac{dX}{dt} = -Ae^{-E/RT}X^n$	(30)
n-order non-isothermal	$y = B + Cx + Dz$	(31)
Calvo et al. [65] *n*-order-independent parallel	$\frac{d\omega_i}{dt} = K_i\, e^{(-E_i/RT)}(1-\omega_i)^n$	(32)
	$\omega_i = \frac{m_{0i} - m_{ij}}{m_{0i} - m_{fi}}$	(33)
	$\frac{d\omega_i}{dT} = \frac{K_i}{q}\, e^{(-E_i/RT)}(1-\omega_i)$	(34)
	$-\frac{d\omega}{dt} = \sum_{i=1}^{n} c_i \frac{d\omega_i}{dt}$	(35)
Sharma and Rao [67] *n*-order	$\frac{dX}{dt} = K(1-X)^n$	(13)
	$X = \frac{(W_0 - W)}{(W_0 - W_\infty)}$	(14)
Gonzalez et al. [63]	$\frac{dX}{dt} = k(1-X)$	(11)
First-order non-isothermal	$-\ln(1-X) = kt$	(12)

5.1.1.1. Isothermal region. As it is mentioned previously, agricultural residues are mixtures which are mainly composed of cellulose, semicellulose and lignin and their decomposition *comprises a large number of reactions in parallel and in series.*

In the isothermal region the most often used models are normally based *on mechanisms involving series–parallel reactions*. These models assume the biomass residue to decompose to each reaction product through *an independent, single and molecular reaction*. First- and *n*-order reactions have been studied.

Kinetic study of *first-order* pyrolysis, based on gas generation from thermal decomposition of residues, under isothermal pyrolysis, has been carried out by researchers [60]. From this model, rate constants for the formation of each gas and their corresponding activation energies were determined. The rate of generation of a gas is given by Eq. (5):

$$r = \frac{d_m}{d_t}, \quad (5)$$

Table 13
Kinetic models for the activation of carbons produced from the pyrolysis

Reference		
Bhat et al. [84] First order	$\frac{dX}{dt} = k_v(1-X)C_{A0}$	(38)
	$-\ln(1-X) = (k_v C_{A0})t$	(39)
	$\rho\left(\frac{-dr_c}{dt}\right) = k_r C_{A0}$	(40)
	$t = \left(\frac{\rho R_p}{k_r C_{A0}}\right)[1-(1-X)^{1/3}]$	(41)
Zolin et al. [90] RPM, VRM	$\text{rate} = \frac{1}{1-X}\frac{dX}{dt} = k_0 e^{-E_a/RT}$	(55)
	$X = (1-F)X_1 + FX_2$	(56)
Klose and Wolki [89] Ergun-Reif	$r_{m,c} = \frac{k_{20}\exp(-(E_{A,2}/RT))}{1+K'_{10}/\exp(-(\Delta_s H_{m,1}/RT)p_{CO_2})}$	(51)
Ollero et al. [85] *n*-order & L-H	$R = -\frac{1}{w-w_a}\frac{dw}{dt} = \frac{1}{1-X}\frac{dX}{dt}$	(42)
	$R_{50} = Kp^n_{CO_2}, \quad K = k_0\exp\left(-\frac{E}{RT}\right)$	(43)
	$R_{50} = \frac{K_1 p_{CO_2}}{1+\alpha p_{CO} + b p_{CO_2}}$	(44)
Barea et al. [87] Non-isothermal, non-equimolar	$\frac{\partial X}{\partial t} = (1-X)R$	(45)
	$R(X) = f(X)R_{50}$	(48)
	$\eta_{cal}(t) = \frac{\iiint v C_{CO}(1-X)R\,dV}{\iiint v C_{CO}(1-X)R_G\,dV}$	(49)

where m represents the number of moles generated. At a given time, t, m can be expressed as

$$m = \int_0^t CF d_t, \tag{6}$$

where C and F are the concentration of the gas at the reactor outlet and the total gas flow rate, respectively.

Table 14
Experimental conditions and kinetic parameters

Reference	Material	Particle size	Sample weight (mg)	Temparature (°C)	Heating rate (°C/min)	Gas/flow rate	Activation energy (kJ/mol)	Pre-exponential factor (s^{-1})	Reaction order
Caballero et al. [58]	Almond shells		3–4	227	2,10,25K/min	N_2/60 ml/min	234.7–254.4	3.007×10^{13} –1.034×10^{18}	1
2-fractions							97.9–118.7	1.259×10^{3}–2.664×10^{6}	1
2-fractions	Olive stones						218.4–222.7	5.922×10^{15}– 1.487×10^{16}	1
							121.5–133	4.654×10^{9}– 6.047×10^{9}	1
Zabaniotou et al. [59]	Olive residues	500 mm	200	300–600	100–300(°C/s)		10.99	0.92	1
				250–400			46.65	4.6	1
Encinar et al. [60]	Olive bagasse	0.4–2 mm	10×10^{3}	300–900		N_2/200 cm^3/min	25.5–79.1	1.67×10^{-5}	1
isothermal-gas generation	Grape bagasse						24.1–98.1		
Cao et al. [61]	Corn cob	60 mesh	50	233–321	5, 10, 30K/min	N_2/80 ml/min	119.6–135.3	8.9×10^{10}–1.09×10^{12}	3–3.2
2 steps				321–385			67.6–176	5.28×10^{6}–3.5×10^{15}	0.34–2
Bonelli et al. [62]	Brazil nut shells	3.7–4.4 × 10^{-5}m diam.	10±0.2	350,600,850,900	15	N_2, CO_2/25 ml/s	47.2	5.7×10^{2}	1
Non-isothermal									
Gonzalez et al. [63]	Cherry stones	0.32–2 mm	10×10^{3}	300–800	5–20 K/min	N_2/200 cm^3/min	107.1	9.83×10^{4}	1
Non-isothermal 3 stages							93.3	1.283×10^{6}	1
							44.7	7.167	1
Isothermal 2 stages				300–600	5–25 K/min		40.1	5.5	1
							48.6	29.6	1
Mansaray, Ghaly [64]	Rice husk	425 µm	10–15	700	20	Pure O_2/50 ml/min	142.7–188.5	1.9667×10^{12}–2.033×10^{15}	0.7–0.83
2 zones							11–16.6	0.05–0.933	0.2–0.29
Calvo et al. [65]	Rice straw-AIM	420 µm	6–9	923	15	N_2-air/100 ml/min	70–83	2.35×10^{6}–6.19×10^{13}	
	Rice straw-DM						85–131	2.54×10^{5}–1.43×10^{10}	0.86–2.39
Sharma and Rao [67]	Rice husk, grain + powder	70 µm	15–20	225–350	5, 10, 25, 50, 100	N_2	72.7–97.1	3.7×10^{5}–1.3×10^{9}	1.5
Non-isothermal	Grain + powder			350–600		N_2	6.3–21.9	8.4×10^{-2}–68.1	2
	Grain			225–375		CO_2	75.3–83.5	2×10^{5}–2.2×10^{7}	1.5
	Grain			375–700		CO_2	4.2–7.1	2×10^{-2}–7.1×10^{-1}	2
Isothermal	Grain			250–350		N_2	33.1	1.7	1.5
	Grain			350–550		N_2	28.3	5.5×10^{-1}	2

Since the reactions are of *first order*, the rate of thermal decomposition for a residue could follow

$$-\frac{d_M}{d_t} = kM, \tag{7}$$

where M is the mass of residue.

In Eq. (7), M can be related to the loss of residue mass (M_0-M) by introducing a coefficient α as follows:

$$m = \int_0^t CF\, d_t = \alpha(M_0 - M), \tag{8}$$

where M_0 is the initial mass of residue to be pyrolyzed. Differentiation of Eq. (5), once Eq. (7) is accounted for, yields:

$$\frac{d_m}{d_t} = -\alpha\frac{d_M}{d_i} = \alpha kM = \alpha k\frac{m - \alpha M_0}{-\alpha} = k(m_0 - m), \tag{9}$$

where $m_0 = \alpha M_0$ represents the total gas moles generated at the time when all possible pyrolysis of the residue is completed, that is, when the residue is exhausted. This value can be obtained from high temperature experiments with reaction times long enough to ensure no evolution of gases. After separation of variables and integration, Eq. (9) becomes:

$$\ln\frac{m_0}{m_0 - m} = kt. \tag{10}$$

According to Eq. (10) a plot of its left side versus time should yield a straight line whose slope is k, the rate constant of gas formation.

Gonzalez et al. have studied the cherry stones [63] with a thermogravimetric method, *isothermally and non-isothermally*. For the *isothermal* experiments, the pyrolysis process consisted of *two stages*. Their simplest model assumes a *first-order* overall decomposition of the reactive part of the solid and the decomposition rate can be expressed as

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k(1 - X), \tag{11}$$

where X is the conversion (ratio between the solid weight loss at a given time and the initial solid weight), k is the kinetic constant, and t is the time. After separation of variables and integration, Eq. (11) becomes

$$-\ln(1 - X) = kt. \tag{12}$$

Sharma and Rao [67] have studied *n-order* reaction model for rice husks, under isothermal conditions. The nth order rate equation is expressed by

$$\frac{\mathrm{d}X}{\mathrm{d}t} = K(1 - X)^n, \tag{13}$$

$$X = \frac{(W_0 - W)}{(W_0 - W_\infty)}. \tag{14}$$

For isothermal kinetics the equations are:

$$F(X) = -\mathrm{Ln}(1 - X) = Kt \;\text{ for }\; n = 1, \tag{15}$$

$$F(X) = \frac{[\{(1-X)^{n-1}\}-1]}{(1-n)} = Kt \text{ for } n \neq 1. \tag{16}$$

5.1.1.2. Non-isothermal region. The heating rate may affect the process of reaction kinetics. Since the order of reaction involved is higher at a slower heating rate, this result suggests that a series of complicated reactions may occur at this condition. In contrast to this, the result that the order of the decomposition reaction is lower at a fast heating rate suggests that the path taken under this condition is simpler. In order to effectively reduce unnecessary reactions through thermal disposal, a fast heating rate should be used [61].

In view of the fact that agricultural residues are mixtures which are mainly composed of cellulose, semicellulose and lignin, their decomposition comprises a large number of reactions in parallel and in series, *whereas DTG measures the overall weight loss* due to these causes. Although TGA provides general information on the overall reaction kinetics, rather than individual reactions, it could be used as a tool for providing comparison kinetic data of various reaction parameters such as temperature and heating rate. Other advantages of determining kinetic parameters from TGA are that only a single sample and considerably fewer data are required for calculating the kinetics over an entire temperature range in a continuous manner.

Many researchers [61] assumed that devolatilization in the kinetic analysis of DTG data was a *first-order* reaction. Indicated by the DTG curves, two values of the activation energy, the reaction order and the pre-exponential factors may be used to describe the mechanism at a certain heating rate. In the study performed by Qing Cao et al. [61] it was shown by DTG that thermal decomposition process involves two steps. The heating rate affects not only the activation energy of the decomposition reaction, but also the path of the reaction. With the increment of the heating rate, the maximum rate temperature of the decomposition reaction was shifted to a higher temperature, and the order and activation energy of the total decomposition reaction were decreasing. In their model it was assumed an *n*-order reaction for the decomposition of residues [61]. Therefore, the rate of decomposition is calculated by the following equation:

$$\frac{d_\alpha}{d_t} = k(1-\alpha)^n, \tag{17}$$

where a is the converted rate of reaction, which is defined as $(w_0-w)/(w_0-w_\infty)$, t is the time, w_0 is the mass of initial sample, w is the mass of actual sample at time t, w_∞ is the mass of residue at the end of the reaction and k is the rate constant, which is also defined by the Arrhenius equation:

$$k = A\mathrm{e}^{(-E/RT)}, \tag{18}$$

where A is the pre-exponential factor and E is the apparent activation energy of the decomposition reaction, R is the ideal gas constant and T is the temperature. The DTG continuous recording of weight loss against time and temperature gives $\mathrm{d}w/\mathrm{d}t$. If heating rate $\beta = \mathrm{d}T = \mathrm{d}t$, the rate of the decomposition equation may be expressed as

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = -\frac{\mathrm{d}w}{\mathrm{d}T} = \frac{A}{\beta}\,\mathrm{e}^{(-E/RT)}(1-\alpha)^n, \tag{19}$$

$$\ln\left(\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln\frac{A}{\beta} - \frac{E}{RT} + n\ln(1-\alpha). \tag{20}$$

If the effect of small changes of temperature on apparent activated energy is neglected, Eq. (20) can be expressed as

$$\Delta \ln\left(\frac{d\alpha}{dT}\right) = -\frac{E}{RT}\,\Delta\left(\frac{1}{T}\right) + n\,\Delta \ln(1-\alpha), \tag{21}$$

$$\frac{[\Delta \ln(d\alpha/dT)]}{\Delta \ln(1-\alpha)} = \frac{[(-E/R)\,\Delta(1/T)]}{\Delta \ln(1-\alpha)} + n. \tag{22}$$

Due to $d\alpha/dT = -(1/w_0 - w_\infty)dw/dT = -(1/\beta(w_0 - w_\infty))dw/dt$, for Eq. (22), all related parameters such as $\Delta\ln(da/dT)$, $\Delta 1/T$ and $\Delta\ln(1-\alpha)$ can be calculated from DTG analysis data. The value of the reaction order n and activation energy E can be obtained through the intercept and slope of a straight line given by a plot of $[\Delta\ln(d\alpha/dT)]/\Delta\ln(1-\alpha)$ versus $[-\Delta(1/T)]/R\Delta\ln(1-\alpha)$. The pre-exponential factor A also can be obtained from Eq. (20), where A/β can be obtained through the intercept of a straight line given by a plot of $\ln(d\alpha/dT)$ versus $[-E/RT + n(1-\alpha)]$ and β is the heating rate, the value designed by experiments. Considering the two prominent steps (lower and higher temperature regions) of the reaction indicated by the DTG curves, two values of the activation energy, the reaction order and the pre-exponential factors may be used to describe the mechanism at a certain heating rate.

As mentioned in the previous paragraph, Gonzalez et al. [63], have studied cherry stones under isothermal and non-isothermal conditions and considered *first-order* reactions. In dynamic conditions (non-isothermal), they investigated pyrolysis consisted of *three stages;* whereas in isothermal condition they have investigated pyrolysis consisted of *two stages*. For non-isothermal conditions the decomposition rate of the feedstock can be expressed as

$$\frac{dX}{dt} = \frac{k_0}{\alpha}\exp\left(-\frac{E_a}{RT}\right)(1-X), \tag{23}$$

where α is the heating rate.

Taking natural logarithms on both sides of Eq. (23) yields

$$\ln\left[\frac{1}{(1-X)}\frac{dX}{dt}\right] = \ln\frac{k_0}{a} - \frac{E_a}{RT}. \tag{24}$$

Some other researchers, Bonelli et al. [62], have used *DMs* considering series–parallel reactions based on DTG-TGA data and linear relationship between temperature and time. They applied DM for Brazil Nut shells' decomposition.

In their model, fitting of TG curves (w vs. T) was carried out taking into account the measured linear relationship between temperature and time, that is given by

$$T = T_{amb} + ut, \tag{25}$$

where T is the instantaneous temperature, T_{amb}, ambient temperature, u the heating rate and t is the reaction time.

A *simple model (SM)* that assumes pyrolysis as a first-order overall decomposition was used. The reaction rate is given by

$$-\frac{dw}{dt} = k(w - w_\infty) \tag{26}$$

and

$$k = k_0 \exp\left(\frac{-E}{RT}\right), \tag{27}$$

where k is the specific rate constant, k_0 the pre-exponential factor, E_a the activation energy, w_∞ the residual mass fraction, R the universal gas constant and T the absolute temperature.

In order to fit experimental data over the whole range of degradation temperatures investigated, namely up to 870 °C, *a DM* proposed in the literature was used. *The DM model assumes a first-order overall decomposition*, as given by Eq. (26), and *considers that the significant physical and chemical changes which take place within the solid as pyrolysis proceeds cause solid deactivation*. This fact affects the reaction rate constant (k_{app}) and is taken into account through an increase of the activation energy with the temperature and the solid conversion according to

$$k_{app} = k_0 \exp\left\{\frac{-E_{a0}(1 + \beta T z^{\gamma})}{RT}\right\}, \tag{28}$$

where z is the normalized fractional conversion

$$z = 1 - \frac{w}{1 - w_\infty} \tag{29}$$

and E_{a0} the initial activation energy, for $z = 0$ and β, γ, fitting parameters (β the deactivation rate, γ the order with respect to z).

In addition to the published studies considering first-order kinetics there are some other studies dealing with *n-order* reactions. Mansaray and Ghaly [64] studied rice husks in pure O_2 using TGA. They have determined kinetic parameters from TGA data, for two reaction zones, based on the following rate expression [64]:

$$\frac{dX}{dt} = -A e^{(-E/RT)} X^n, \tag{30}$$

where X is the weight of sample undergoing reaction (kg); t the time (min), A the pre-exponential or frequency factor (min^{-1}), E the activation energy of the decomposition reaction (kJ mol^{-1}), R the universal gas constant (kJ mol^{-1} K^{-1}), T the absolute temperature (K), and n the order of reaction (–).

A technique based on the Arrhenius equation was used to determine the kinetic parameters from typical curves of thermogravimetric data over an entire temperature range in a continuous manner. The linearized form of the Arrhenius equation was used to determine A, E and n by applying least squares (multiple linear regression) technique. The simplified form of the linearized rate equation is as follows:

$$y = B + Cx + Dz. \tag{31}$$

The parameters y, x, z, B, C and D in Eq. (31) are defined as follows:

$y = \ln\{[-1/(w_0 - w_f)][dw/dt]\}$,
$x = 1/(RT)$,
$z = \ln\{(w - w_f)/(w_0 - w_f)]$,
$B = \ln A$,
$C = -E$,
$D = n$.

Calvo et al. [65] have based their study on *n-order* reactions, for rice straw pyrolysis. They considered also, *several components, which presumably decompose independently of one another*, so the best mathematical models for describing overall decomposition consider *independent parallel reactions.* They also used DTG curves for two models: in the *first model* (AIM) it was *assumed that the reaction is a simple first-order one*.; In the *second model* (DM) it was *assumed that the reaction is a simple n-order one*. The kinetic equations for each single reaction were

$$\frac{d\omega_i}{dt} = K_i\, e^{(-E_i/RT)}\,(1-\omega_i)^n, \tag{32}$$

$$\omega_\imath = \frac{m_{0i}-m_{ij}}{m_{0i}-m_{\mathrm{fi}}} \tag{33}$$

where x_i is the reacted mass fraction or normalized mass for reaction i at time j; t is time; R is the gas universal constant; T is the absolute temperature; K_i is the frequency factor; E_i is the activation energy; n is the order of reaction; $m_{0\mathrm{i}}$ is the initial mass of the sample i; m_{ij} is sample mass for the reaction i at time j and m_{fi} is final mass of the sample in that reaction.

In the *first model* (AIM) where it was *assumed that the reaction is a simple first-order one*, for a constant heating rate, Eq. (32) can be written as

$$\frac{d\omega_i}{dT} = \frac{K_i}{q}\, e^{(-E_i/RT)}\,(1-\omega_i), \tag{34}$$

where q is the constant heating rate.

In the *second model* (direct method, DM) it was assumed that the components of the sample decompose independently of one another, so the overall rate of conversion for N reactions can be described by

$$-\frac{d\omega}{dt} = \sum_{i=1}^{n} c_i\,\frac{d\omega_i}{dt}, \tag{35}$$

where c_i is a coefficient that expresses the contribution of each single reaction to the mass global loss.

Generally, the direct method was more complete as it could calculate the activation energy, the frequency factor for the differential stages in the thermal process and the order of the reaction. However, the first one had the advantage of simplicity.

Sharma and Rao [67] have studied *n-order* reaction model for rice husks. In the study of the experiments took place under both isothermal as described in the previous paragraph, and non-isothermal data. The nth-order rate equation is expressed by Eqs. (13) and (14).

For *non-isothermal kinetics* the final equation is

$$\mathrm{Ln}[F(X)] = -\frac{E}{RT} + \mathrm{Ln}\left[\left(\frac{AR}{\beta E}\right)\left(1-2\frac{RT}{E}\right)\right]. \tag{36}$$

5.1.2. *ASEM (semi-empirical model)*

As said above, the number of reactions that occur simultaneously in the most simple pyrolysis process is so great that it is practically impossible to develop a kinetic model that takes into account all these reactions. To overcome this difficulty, pyrolysis is usually studied in terms of *semi-empirical model.*

In the corn stover study of researchers, Green and Feng from China [66], *the time independent ASEM methodology* was applied for the organization of the pyrolysis yield data. The same data were also organized with a traditional kinetic model, which, though, was not very effective.

With the analytical *semi-empirical model* the yields of all products were represented by

$$Y(T) = W[L(T)]^p[F(T)]^q, \tag{37}$$

where

$$L(T) = \frac{1}{[1 + \exp Z]}, \quad Z = \frac{T_0 - T}{D}$$

and

$$F(T) = 1 - L(T) = \frac{1}{1 + \exp X}, \quad X = -Z = \frac{T - T_0}{D}.$$

5.1.3. Modelling coupling kinetics and transport phenomena in a single biomass particle

Another classification of biomass pyrolysis can be made by incorporating transfer phenomena with the chemical kinetics equations. Fan et al. [68] developed a model for pyrolysis process, which includes heat and mass transfer in the particle. Miyanami et al. [69] incorporated the effect of heat of reaction in the above model. Bamford et al. [70], has combined the above model with heat generation and then Kung [71], has modified it in order to incorporate the effects of internal convention and variable transport properties. Kansa et al. [72], included the momentum equation for the motion of pyrolysis gases within the solid and pointed out that secondary reactions are essential to fully match the experimental observations. Koufopanos et al. [73], have introduced an empirical correlation of thermal properties considering being linear functions of temperature and conversion. Many researchers have studied pyrolysis of biomass solid particle considering secondary reactions [74–77] pointed out that a detailed transport model incorporating kinetics and heat and mass transfer effects is necessary to predict the effects of widely variable physical properties in the pyrolysis of biomass. Larfeldt et al. [78] have performed studies on the influence of particle structure and heat transfer characteristics on the pyrolysis of *large wood particles*. Boutin et al. [79] have studied flash pyrolysis of cellulose pellets.

All the above models have based on conservation of mass, energy and species on a differential basis within the solid and gas phase portions of the porous medium. *Char shrinkage* is not addressed in these models. The shrinking of the solid particle affects the pyrolysis in several ways. The medium properties (porosity, permeability, density, mass diffusivity, specific heat capacity and thermal conductivity), the volume occupied by the solid (wood and char) and consequently the total volume of the particle also changes continuously. As a result of the chemical restructuring during pyrolysis, the density of the char increases. The temperature profile of the particle changes due to increased density and decreased distance across the pyrolysis region [80]. The product yield is also affected by the thinner and hotter char layer [81]. Bryden and Hagge [81] have studied first a detailed model of moist wood pyrolysis for non-shrinking particles and then they have expanded to include shrinkage of the solid matrix due to pyrolysis for dry wood particles. In their study [81], it was found that shrinkage has a negligible effect on pyrolysis in the thermally thin pyrolysis regime. Colomba di Blasi [82] has studied transport phenomena through a

shrinking biomass particle. Bellais et al. [83] have studied the pyrolysis of large wood particles and shrinkage importance in simulations. Babu and Chaurasia [80] have also studied heat transfer and kinetics in the pyrolysis of shrinking biomass particle.

During the pyrolysis of a large biomass particle a charcoal layer is developed at the surface of the particle. Since the thermal conductivity of the char is less than that of wood the heat transfer through this layer becomes limiting for the rate of pyrolysis of the interior biomass particle [78]. According to Larfeldt et al. [78], the conductivity increases with temperature only due to the increase in gas phase conductivity with temperature and due to radiation in pores. A more detailed knowledge of the pore size distribution in the charcoal is required. It is considered that the microstructure is related to the structure of a virgin wood, whereas the macro pores is formed during pyrolysis. Thus the macro structure depends on the pyrolysis process such as heating rate, particle size and moisture content [78].

5.2. *Kinetic models for activation*

From the process design viewpoint, it is important to know the reaction and pore structure evolution. Although few models regarding the kinetics of agricultural char activation are currently available, different models proposed for char derived from various precursors such as coal or tires.

For the activation of the char issued from agricultural residues, TGA method was used by many researches [84–88] as presented in Table 13. In the study of Bhat et al. [84], rice husk char was gasified with steam and CO_2 and the data were analysed by two models, the *homogeneous* and the *shrinking core* one.

From the weight loss vs. time data [84], the fractional conversions with respect to time are calculated, taking into consideration of the composition of the char as determined by the proximate analysis. The rate equations used for determining the kinetic parameters are as follows:

5.2.1. *Volume reaction model /homogeneous*

$$\frac{\mathrm{d}X}{\mathrm{d}t} = k_v(1 - X)C_{\mathrm{A0}}, \tag{38}$$

$$-\ln(1 - X) = (k_v C_{\mathrm{A0}})t. \tag{39}$$

5.2.2. *Shrinking core model*

$$\rho\left(\frac{-\mathrm{d}r_c}{\mathrm{d}t}\right) = k_r C_{\mathrm{A0}}, \tag{40}$$

$$t = \left(\frac{\rho R_p}{k_r C_{\mathrm{A0}}}\right)[1 - (1 - X)^{1/3}]. \tag{41}$$

In a study of Ollero et al. [85], as in other studies of Shim et al. [86] and Ollero et al. [88] too, the reactivity R (s^{-1}) is defined as

$$R = -\frac{1}{w - w_{\mathrm{a}}}\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{1}{1 - X}\frac{\mathrm{d}X}{\mathrm{d}t}, \tag{42}$$

where w is the weight of the char, w_a the weight of the ash, X the degree of conversion, $X = (w_0 - w)/(w_0\, w_a)$, where w_0 is the initial weight of the dried and pyrolysed sample. For biomass chars, reactivity increases with increasing conversion.

The *n*th *order kinetics* is often adopted when CO is absent, and expresses the temperature and CO_2 pressure dependence of the representative reactivity. Hence

$$R_{50} = Kp^n_{CO_2}, \quad K = k_0 \exp\left(-\frac{E}{RT}\right). \tag{43}$$

Using the *Lanqmuir–Hinshelwood kinetic equation*, the reactivity is expressed as

$$R_{50} = \frac{K_1 p_{CO_2}}{1 + \alpha p_{CO} + b p_{CO_2}}, \tag{44}$$

where K_1, α and b are kinetic parameters that depend only on the temperature. The same kinetic models were used in the study of Ollero et al. [88].

Some other models consider also transport phenomena. Gomez et al. [87] have used in their model a chemical reaction rate taking into account and *pseudo-steady state* hypothesis assuming gas mass and heat transfer. The molar balance for the char is [88]

$$\frac{\partial X}{\partial t} = (1 - X)R, \tag{45}$$

where X is the degree of conversion defined as the ratio of the instantaneous weight of the char sample to the initial weight of the sample, both ash free.

Molar balance of the gaseous reactant CO_2 and product CO (throughout what follows component A and B, respectively):

$$\nabla \cdot N_A + C_{CO}(1 - X)\, R = 0, \tag{46}$$

$$\nabla \cdot N_B - 2C_{CO}(1 - X)\, R = 0, \tag{47}$$

where N_A and N_B are the molar fluxes of CO_2 and CO and C_{C0} is the initial carbon molar bulk density of the sample.

The *heterogeneous gas–solid* reaction mainly takes place on the inner surface of the char particles. The reactivity at any conversion may be written according to

$$R(X) = f(X)R_{50}, \tag{48}$$

where *f*(X) is a normalized structural profile.

The effectiveness factor is a good measure of the mass and heat transfer effects during the gasification process in a TGA. According to its definition, the model calculates the effectiveness factor at any time by means of the expression,

$$\eta_{cal}(t) = \frac{\iiint v C_{CO}(1 - X)\, R \, dV}{\iiint v C_{CO}(1 - X)\, R_G \, dV}, \tag{49}$$

where V is the volume of the system, which includes the stagnation gas and the char bed model zones.

In the kinetic studies [89], the gasification of the char with CO_2 and steam was studied *isothermally* and the reaction rate was determined as a function of *partial pressure* of the gasifying agent and the reaction temperature. The reaction conditions were determined by varying the particle size, flow rate and the amount of char. The reaction rate was based on the Langmuir–Hinshelwood type rate expression that was used for two reactions and

non-linear regression for the gasification of biomass chars with carbon dioxide and steam:

$$r_{m,c} = \frac{k_{20}\,\exp(-(E_{A,2}/RT))}{1 + (K'_{10}/\exp(-(\Delta_s H_{m,1}/RT))p_{CO_2})}, \tag{50}$$

$$r_{m,c} = \frac{k_{40}\,\exp(-(E_{A,4}/RT))}{1 + (K'_{30}/\exp(-(\Delta_s H_{m,3}/RT))p_{H_2O})}, \tag{51}$$

$$K'_{01} = \frac{P_{CO}}{K_{01}} \approx const. \tag{52}$$

$$K'_{03} = \frac{P_{H_2}}{K_{01}} \approx const. \tag{53}$$

A Random Pore Model (RPM) was used by Zolin et al. [90]. The rate in study [90] was given by

$$\text{rate} = \frac{1}{1-X}\frac{dX}{dt} = k_0 e^{-E_a/RT}, \tag{54}$$

where rate (mg/mg s) represents the reaction rate based on the instantaneous weight of the char; $X = 1 - W/W_0$ is the char conversion on a daf basis, as defined earlier; k_0 (s^{-1}) is the pre-exponential factor; E_a(kJ/mol) the activation energy for char oxidation; R (kJ/mol K) the gas constant and the T the reaction temperature.

For the particular case of the TGA chars, the overall char conversion was calculated from:

$$X = (1-F)X_1 + FX_2, \tag{55}$$

where

$$X_i \cong 1 - \exp\left(-\frac{1}{\alpha}T^2\frac{R}{E_{a_i}}k_i e^{-(E_{a_i}/RT)}\right), \quad i = 1, 2, \tag{56}$$

$i = 1$ represents the reactive phase and $i = 2$, the less reactive phase; X_i is the conversion; F the weight fraction of the less reactive phase; α the heating during the oxidation experiments; k_i the pre-exponential factor (s^{-1}) of the respective phase; E_{a_i} the activation energy (kJ/mol) and T is the reaction temperature (K).

6. Conclusions

6.1. Concerning type of agricultural residues

- The differences in the ultimate and elemental analysis of activated carbons produced from different raw materials, under the same conditions, indicate the dominant influences of the composition and structure of the precursors on their reactivity in the pyrolysis/activation reactions.
- Pyrolysis of agricultural residues, including wheat, straw, olive husks, grape residue, rice husks, etc, *produce char up to twice the yield of char issued from wood.*

- Activated carbons from *almond shell, nut shell, apricot and cherry stones*, have *low ash content* in contrast with the carbon from *grape seeds* which has relatively *high ash content*. All samples have *low sulphur con*tent. The following order of suitability of raw materials for activated carbon production was established: hazelnut shell > apricot stone > almond shell.
- The higher yields of activated carbons with high BET obtained from olive wastes, birch and bagasse, make these raw materials suitable for preparation of activated carbon while samples from straw and miscanthus seem more suitable for conversion into liquid and gaseous products.

6.2. Concerning process parameters

- Characteristic of char is dependent on the *pyrolysis conditions*. Both the hydrogen and oxygen contents of char decrease as the temperature is increased. H/C ratio decreases indicating an increase in the aromaticity and carbonaceous nature of char.
- BET surface area and the total pore volume increase with *pyrolysis temperature*, and reach a maximum at about 500 °C; thereafter, the trend is a decrease with pyrolysis temperature. The rate of declination is not as fast as that of increase. However, increase in temperature from 500 to 800 °C may induce shrinkage in the carbon structure, resulting in a reduction in the surface area and the pore volume.
- Total pore volumes are generally increased with *time*. As activation proceeds all kinds of porosity are increasing. The results indicate that the produced carbons show higher adsorption capacities and higher surface areas than the commercial type.
- Moreover, it seems that the *soaking time in the chemical activation* plays a less important role in the production of activated carbon. It is seen that, by increasing soaking time, the surface area and the pore volume were increased as a result of the development of porosity. However, the values thereafter are observed to decrease gradually at longer soaking time, which is possibly attributed to the gasification of the few well developed micropore wall.
- For the agricultural waste of cotton stalk pyrolysis yields are strongly dependent on *temperature* but independent of *particle size* and *nitrogen flow rate*.
- BET surface areas from olive-seed-based activated carbon not only are increasing with activation time and temperature, but they also show an increase with an increase of *the burn-off*, which proved to be the most significant factor, regardless of the activation temperature.

6.3. Concerning type of activation

- *Steam pyrolysis* of raw material produces a larger development of porosity than activation with water vapour of material carbonized in N_2.
- The experimental results of Macadamia nutshells show that surface area and micropore volume of the samples produced by chemical activation with $ZnCl_2$ are much higher than those with *KOH*. High-quality of carbon can easily be produced from peanut hulls through chemical activation with H_3PO_4 at 500 °C.
- *Chemical activation* of pecan shells generated *granular* activated carbons with large surface area.

- *Sugarcane* bagasse showed a better potential than *rice straw* or *rice hulls* as precursor of *granular* activated carbons with the desirable properties.

6.4. Concerning uses of active carbons

- Activated carbon surfaces have a pore size that determine its adsorption capacity, a chemical structure that influences its interaction with polar and non-polar adsorbates, and active sites which determine the type of chemical reactions with other molecules. Conversion of plentiful by-products into activated carbons that can be used in applications such as drinking water purification, waste treatments, treatment of dyes and met al-ions from aqueous solution would add value to agricultural commodities, help the agricultural economy with an additional market potential, offer solution to environmental problems and help reduce the cost of waste disposal. As the raw materials obtained from agricultural wastes are available freely and abundantly, the cost for preparation of carbons is expected to be low and provide a potentially inexpensive replacement of existing commercial adsorbents from non-renewable sources.
- Generally, the activated carbons produced from fruit shells and stones have high surface areas and highly developed micropore structure than the commercial and those issued from used tires.
- Activation time and temperature had an influence on phenol and methylene blue adsorption especially for activated carbon from hazelnut.
- Activated carbons prepared with the pistachio-nut shells can be used for both gas and liquid adsorption applications, depending on the activation conditions. Peanut husks carbon is an effective adsorbent for the removal of Pb^{2+}, Cd^{2+}, Zn^{2+} and Ni^{2+} from aqueous solutions. It would be useful for the economic treatment of wastewater containing these heavy metals, as the adsorbent has a much superior capacity to the commercial activated carbon.
- Copper-impregnated coconut husk carbon can be used as an adsorbent for the effective removal of As(III) from aqueous solutions.
- The carbonized product from beet pulp is an efficient adsorbent for the removal of phenol from aqueous solution.
- Three grades of carbons were obtained from *corn cobs:* (a) *Those* obtained by carbonization yields a poorly developed wide-pored carbon with capacity for iodine and Pb^{2+} ions; (b) steam-activated carbons (in one or two step schemes) develop porosity with temperature, and are essentially microporous. These exhibit good adsorbing affinity from solution (iodine, phenol, and methylene blue) that depends on their porosity characteristics; (c) chemical activation by H_3PO_4 at 500 °C proved very effective in producing high quality activated carbon with well-developed porosity and high adsorption capacity for both organic and inorganic substrates.
- A binary mixture of carbons from acid-activated almond and steam-activated pecan were the most effective in removing the metals copper (Cu^{2+}), lead (Pb^{2+}) and zinc (Zn^{2+}), from drinking water of all the POU systems (point-of-use) evaluated.
- Almond shell-based carbon with steam-activated pecan shell- removed nearly 100% of lead ion, 90–95% of copper ion and 80–90% of zinc ion. Acid activation resulted in higher yield, lower surface area, higher percentage of micropore compared to steam activation. Percent yield is a factor used in cost estimation and commercial potential of activated carbons.

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